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URBANA

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WATER SOLUBLE SALTS IN LIMESTONES AND DOLOMITES

By
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WATER SOLUBLE SALTS IN LIMESTONES AND DOLOMITES.*

J. E. LAMAR AND RAYMOND S. SHRODE.

ABSTRACT.

Samples of representative Illinois limestones and dolomites were ground in distilled water and the amount of water-soluble salts in the resulting leaches was determined by chemical analysis and by weighing the leach solids resulting from evaporating the leaches. The dolomite leaches contained more soluble salts on an average than the limestone leaches and commonly contained the more Mg^{++}, HCO_3^-, and Cl^-. The limestone leaches generally exceeded the dolomites in Ca^{++} and SO_4^{--}. X-ray diffraction data on the leach solids from the limestones showed that they are generally characterized by the presence of calcium sulfate, calcium carbonate and sodium chloride. Distinctive compounds of dolomite leach solids are magnesium chloride and basic magnesium carbonate; magnesium sulfate and potassium chloride are found more commonly than in limestone leach solids.

The leaches from dolomites were generally slightly more basic than those from limestones. The calcium sulfate in the leaches may come largely from the solution of inter-crystal deposits of this compound, but the other salts probably come mostly or entirely from intra-crystal fluid inclusions. These inclusions are smaller but more numerous in the dolomites than in the limestones.

Conclusions regarding the occurrence of the water-soluble salts are based on a combination of evidence from thin sections, decrepitation tests, fetid limestone, and efflorescence data.

Water soluble salts have potential economic significance in connection with lime-burning and the physical properties of lime, the uses of limestone and dolomite powders, and the durability of building stone.

INTRODUCTION.

The presence of water-soluble salts in limestones and dolomites has been recognized by some geologists and by certain commercial users of these rocks, but information is scanty regarding the amount and character of such salts. Most attention has been given to the subject in connection with the efflorescence of building stone. Kessler and Sligh [1] report that the efflorescence leached from blocks of limestone with pure water was mainly calcium and magnesium sulfates. Schaffer [2] found that the water-soluble materials in the "florescence" resulting from the weathering of a magnesium limestone consisted of 50 per-

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[1] Kessler, D. W., and Sligh, W. H., Physical properties of the principal commercial limestones used for building construction in the United States: U. S. Bur. Standards, Tech. Paper, vol. 21, No. 349, p. 542, 1927.

[2] Schaffer, R. J., The weathering of natural building stones, Dept. of Scientific and Industrial Research, Building Research, Special Report No. 18, p. 60 (British). 1932.

cent calcium sulfate and 11 percent magnesium sulfate. Anderegg and Peffer [3] percolated water through granulated "Indiana limestone" and found traces of calcium sulfate and magnesium sulfate in the leach. Warnes [4] records the presence of traces of chlorides and sulfates in the efflorescence of limestones. Krotov [5] states that the presence of sodium chloride in dolomites has been "verified by many tests." Berg [6] reports the presence of small amounts of chlorides in dolomites, de Quervain [7] cites the effects of soluble chlorides and sulfates on building stones, and Dahlblom [8] mentions the occurrence of liquids composed of sodium chloride and calcium chloride in otherwise dry rocks, though he does not specify that the rocks are limestones or dolomites.

This paper gives the results of an exploratory investigation of water-soluble salts in calcareous rocks and deals with a representative group of Illinois limestones and dolomites. It is concerned primarily with the amount of soluble salts, their chemical composition, and their mode of occurrence. The constancy of these three factors with respect to lateral variation in a given stratum, vertical variation in a given deposit or geologic formation, and variation between geologic formations of different ages was investigated only briefly and is being studied further.

PROCEDURE.

Preliminary consideration of possible modes of occurrence of water-soluble salts in dry samples suggested that they might occur as solids either in pores or between or within the crystals of the limestone or dolomite, as fluid inclusions within the crystals of the rocks, or as both. Because leaching of the soluble salts in the laboratory by percolating water through samples appeared likely to be a very slow operation, the following procedure was adopted: 600-gram samples of minus 10-mesh stone were ground for 12 hours in 1,500 cc of boiled distilled water in a ball mill jar charged with 2,500 grams of 3/4 inch flint pebbles. The jar was rotated for 12 hours at a rate of 45 rpm. The liquid and solid portions of the resulting slurry were separated by filtration. The liquid is referred to as the "leach," and the solids resulting when the leach was evaporated to dryness as the "leach solids." Some of the leach was analyzed chemically and some was evaporated to dryness to yield leach solids that were cooled in a desiccator and weighed immediately on removal from the desiccator. Later the leach solids were examined by x-ray.

The above procedure fails to give full weight to the fact that some of the samples yielded finer powders than others during the 12-hour grinding period,

[3] Anderegg, F. O., and Peffer, H. C., Indiana limestone—I, Efflorescence and staining: Purdue Univ. Eng. Exp. Station, Bull. 33, p. 17–18, 1928.

[4] Warnes, A. R., Building stones, their properties, decay and preservation: London, p. 189, 1926.

[5] Krotov, B. P., The necessity of a physiochemical study of the reaction $2CaCO_3 + MgSO_4 \rightleftarrows CaCO_3 \cdot MgCO_3 + CaSO_4$: Univ. of Kassan, Ann. inst. anal. phys.-chim. (Leningrad), vol. 3, pp. 662–682; Chem. zentr. 1927, II, p. 2659–60: Chem. Abs. vol. 22, 1928, p. 4417.

[6] Berg, L. G., Influence of salt admixtures upon dissociation of dolomite: Comptes Rendus (Doklady) de l'Academie des Sciences di l' U.R.S.S., vol. 38, no. 1, 1943, p. 26.

[7] de Quervain, F., The effects of weathering on building stones: Mitt. naturforsch, Ges. Bern 8, Sitzber. V-VI, 1951.

[8] Dahlblom, Th., The permeability of rocks: Economic Geology, vol. XIX, 1924, p. 390.

and thus might be expected to give up a larger percentage of their soluble salts. Experiments indicate that this is the case and that grinding for more than 12 hours probably would release additional salts from most or all of the samples. Limited data suggest that the amount of salts released by additional grinding is usually comparatively small, and that the salts are similar to those freed during the 12-hour period. No correlation was found between the fineness of the powders from different samples at the end of the 12-hour grinding period and the amount of soluble salts. The 12-hour period was chosen as one of convenient duration giving reasonably duplicable results.

Checks of the method to determine duplicability of results on the same sample indicate a maximum variation of about ±15 percent. Two samples from the same bed and 300 feet apart showed a maximum variation of 20 percent. In terms of actual weight of leach solid, these variations are small.

Although the leaching procedure described above was deemed adequate for this exploratory study, a more accurate method for recovering the water-soluble salts from calcareous rocks is desirable and is being developed for use in future investigations.

TABLE 1.

SAMPLE DATA AND PERCENTAGE OF LEACH SOLIDS.

Sample no.	Formation	Leach solids (10), percent	Sample no.	Formation	Leach solids (10), percent
	Pennsylvanian			Devonian	
29	Livingston limestone (1)	.048	15	Wapsipinicon limestone (1)	.045
28	LaSalle limestone (1)	.050	14	Grand Tower limestone (2)	.045
27	Brereton limestone (1)(4)	.275	13	Bailey limestone (1)(5)	.085
	Mississippian (upper)			Silurian	
26	Kinkaid limestone (1)	.068	12	Racine dolomite (2)(4)	.330
25	Glen Dean limestone (2)	.115	11	Racine dolomite (2)(8)(9)	.219
24	Okaw limestone (2)	.105	10	Racine dolomite (2)(9)	.323
			9	Racine dolomite (1)(8)	.195
	Mississippian (lower)				
23	Ste. Genevieve limestone (3)(6)(7)	.070		Ordovician	
			8	Kimmswick limestone (3)(8)	.320
22	Ste. Genevieve limestone (1)(6)(7)	.070	7	Kimmswick limestone (3)(8)	.128
			6	Galena dolomite (2)	.155
21	St. Louis limestone (1)	.050	5	Galena dolomite (2)	.175
20	Salem limestone (2)(6)	.038	4	Platteville dolomite (2)	.203
19	Salem limestone (2)	.065	3	Shakopee dolomite (1)(5)	.156
18	Salem limestone (2)	.098	2	Oneota dolomite (2)	.220
17	Burlington limestone (3)(7)	.080			
16	Burlington limestone (1)(7)	.058		Cambrian	
			1	Trempealeau dolomite (2)	.123

(1) Fine-grained.
(2) Medium-grained.
(3) Coarse-grained.
(4) Impure.
(5) Siliceous.
(6) Oolite.
(7) From vertically adjacent beds of same formation.
(8) Samples 9 and 11 are from the same dolomite deposit; samples 7 and 8 are from the same limestone deposit. All other samples are from well separated deposits except those marked (7).
(9) Reef type dolomite.
(10) Weight percent of original rock sample.

SAMPLES.

The samples studied include rock from most of the principal limestone and dolomite formations exposed in Illinois. Geologic data are given in Table I. All samples were fresh rock from quarries, mines, or roadcuts, throughout the state.

TABLE 2.

WATER-SOLUBLE SALTS IN WEIGHT PERCENT OF ROCK.[1,2]

Sample no.	Chemical analyses of leaches—%							Total
	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	SO_4^{--}	Cl^{-}	
27	.031	.017	.009	.008	.019	.132	.007	.223
26	.009	.003	.004	.003	.023	.016	.005	.063
24	.016	.003	.009	.002	.016	.039	.011	.096
23	.007	.000	.009	.002	.009	.008	.017	.052
22	.011	.001	.005	.002	.008	.022	.008	.057
21	.009	.000	.004	.002	.008	.009	.003	.035
18	.015	Tr.	.015	.002	.008	.016	.027	.083
17	.012	.000	.015	.002	.008	.004	.030	.071
16	.005	.001	.008	.002	.011	.001	.015	.043
15	.009	.000	.004	.001	.015	.010	.003	.042
13	.007	.004	.004	.006	.033	.012	.004	.070
11*	.004	.034	.016	.004	.035	.006	.100	.199
9*	.004	.031	.007	.005	.059	.040	.041	.187
8	.062	.012	.007	.002	.008	.184	.011	.286
6*	.002	.021	.015	.003	.057	.006	.039	.143
4*	.006	.027	.009	.006	.039	.077	.025	.189
3*	.007	.024	.009	.004	.066	.024	.023	.157
2*	.004	.027	.024	.004	.046	.036	.063	.204
1*	.003	.016	.012	.002	.058	.008	.024	.123
Average, limestones	.017	.003	.008	.003	.014	.038	.012	.093
Average, dolomites	.004	.026	.013	.004	.051	.028]	.045	.172

[1] Analyses by L. D. McVicker, Chemist, Analytical Division, Geochemical Section, Illinois State Geological Survey.

[2] The chemical composition of the leaches in parts per million can be found by multiplying the data in this table by 4,000. The accepted solubility of calcite in CO_2 free water would give rise to about 6 ppm of Ca^{++}.

* Dolomite.

RESULTS OF TESTS.

Table 1 shows the amount of leach solids, in terms of percent by weight of the original rock sample, obtained from 29 samples. Chemical analyses for the leaches from 19 of the samples listed are given in Table 2.

SIGNIFICANCE OF LEACH SOLID AND CHEMICAL DATA.

The totals of the chemical analyses of the leaches of the samples (Table 2) are commonly smaller than the weight of the leach solids for the same samples. X-ray data, given later, suggest that the ions determined in the chemical analyses are the principal ones in the leaches and that some of the substances in the leach solids contain considerable amounts of water of crystallization. Because it is not known how much water, if any, was chemically combined with those water-soluble salts which may have occurred naturally as solids, neither the leach solid data nor the chemical data give a necessarily exact figure on the weight percent of soluble salts in the natural rocks. Probably the leach-solid data give an approximate figure on water-soluble salt content; the total of the chemical analyses appears likely to be nearer to the true anhydrous value.

TABLE 3.

X-RAY DATA ON LEACH SOLIDS; IN PROPORTIONAL PARTS.†‡

Sample no.	$CaCO_3$	$Mg(OH)_2 \cdot 2\,MgCO_3$	$CaSO_4$	$MgSO_4$	NaCl	KCl	Other
29	1	—	1	—	1	—	—
27	<1	—	2	2	<1	—	—
26	2	—	2	—	1	—	—
24	<1	—	2	1	2	—	—
23	1	—	2	—	3	?	—
22	<1	—	2	—	1	—	—
21	2	—	<2	—	1	—	—
20	1	—	1	—	2	—	—
18	<1	—	2	—	3	—	—
17	<1	—	<1	—	3	?	—
16	<1	—	—	—	2	<1	—
13	1	—	—	—	1	—	a
12*	—	—	—	1	—	—	—
11*	<1	2	—	—	1	—	$MgCl_2$—4
9*	2	2	—	—	1	<1	—
8	—	—	10	—	1	—	—
6*	—	2	—	—	2	—	a
5*	—	2	—	—	2	<1	a?
4*	<1	—	—	4	2	—	—
3*	<1?	2	—	2	2	<1	—
2*	—	1	—	—	2	<1	a?
1*	<1	2	—	—	2	—	—

a Unidentified substance in recognizable quantity.
? Presence probable but not certain.
* Dolomite.

† The actual hydration state in which hydrous components existed in the individual leach solid samples is omitted from this tabulation.

‡ X-ray identifications reported in this table and at other places in this paper were made by Dr. W. F. Bradley, Chemist and Head, Division of X-ray, Geochemical Section, Illinois State Geological Survey.

The chemical analyses of the leaches reveal the presence of an appreciable amount of carbonate ion, which was analytically determined as HCO_3^-. Some of this bicarbonate may have been present in the rock samples, but it is thought more likely that some calcite and dolomite of the samples themselves may have been dissolved by CO_2 in the water used to process the samples, even though boiled distilled water, presumably containing little CO_2, was used.

X-RAY DATA.

Results of x-ray diffraction studies of the leach solids from most of the samples listed in Table 1 are given in Table 3. The compounds indicated are the major components of the leach solids, as only in favorable cases can a minimum of 5 percent of a substance be recognized by the x-ray procedures used. Calcium chloride probably was present in a number of the leach-solid samples but because the samples were not protected from atmospheric moisture, the chloride doubtless hydrated and became fluid and thus was not found by the diffraction procedure.

EVALUATION OF RESULTS OF TESTS.

Chemical and X-ray Data.—The chemical data given in Table 2 are summarized in Tables 4 and 5. The limestone leaches generally contain more calcium and sulfate ion than the dolomite leaches. Dolomite leaches commonly have more magnesium, bicarbonate and chloride ion than the limestone leaches. Potassium and sodium are about the same in both types of rock. The amount of total water-soluble salts, as shown by chemical analysis and by leach solids, is greater for dolomites than for limestones; but the range in values is greater for limestones. The amount of probable water of crystallization in the leach solids and of compounds not determined in the chemical analyses is a little greater in limestones than dolomites as is also the range in amounts.

The x-ray data (Table 3) indicate that the leach solids of limestones usually

TABLE 4.

SUMMARY OF LEACH ANALYSIS DATA.

	Limestone			Dolomite		
	Max.	Min.	Avg.	Max.	Min.	Avg.
	Weight percent of rock			Weight percent of rock		
Ca^{++}	.062	.005	.017	.007	.002	.004
Mg^{++}	.012	.000	.003	.034	.016	.026
Na^+	.015	.004	.008	.024	.007	.013
K^+	.008	.001	.003	.006	.002	.004
HCO_3^-	.033	.008	.014	.066	.035	.050
SO_4^{--}	.184	.001	.038	.077	.006	.028
Cl^-	.030	.003	.012	.100	.023	.045

TABLE 5.

SUMMARY OF PERCENTAGE COMPOSITION OF LEACHES IN TERMS OF TOTAL IONS REPORTED IN CHEMICAL ANALYSES.

	Limestone			Dolomite		
	Max.	Min.	Avg.	Max.	Min.	Avg.
	Percent			Percent		
Ca^{++}	26	10	17	4	1	2
Mg^{++}	8	0	3	17	13	15
Na^{+}	21	2	10	12	4	8
K^{+}	9	1	4	3	2	2
HCO_3^{-}	46	3	21	46	17	31
SO_4^{--}	64	2	30	41	3	17
Cl^{-}	42	3	15	51	13	25

contain calcium sulfate, calcium carbonate, and sodium chloride. Leach solids of dolomites characteristically contain basic magnesium carbonate, and a more common presence of magnesium sulfate and potassium chloride. They also contain sodium chloride and calcium carbonate.

Grain Size and Amount of Soluble Salts.—In general the amount of leach solids increases with the grain size of the limestone samples, excluding impure limestones, although there are some exceptions (Tables 1, 2). The average weight percent of leach solids from seven fine-grained limestones was 0.056 percent, from six medium-grained samples 0.078 percent and from four coarse-grained samples 0.150 percent. The chemical analysis totals show the same relation between fine- and medium-grained limestones, but the data on the coarse-grained samples resemble those of the fine-grained limestones.

The grain size of the dolomites did not vary enough to allow conclusions regarding the relation between grain size and the amount of water-soluble salts.

Relation Between Amount of Leach Solids and Chemical Data.—The relation between the weight percent of leach solids and the weight percent of water-soluble salts indicated by the totals of the chemical analyses is of interest as the latter data are probably somewhat more exact because they do not involve water of crystallization. Comparison of data on the foregoing in Tables 1 and 2 shows that the weights of the components of the leaches, as indicated by the totals of the chemical analyses, are with one exception smaller than the amount of leach solids. For the limestone samples, weights obtained by chemical analysis range from 70 to 90 percent of the weights of the leach solids and average 85 percent. The range for the dolomites is 92 to 100 percent, and the average is 94 percent.

Water-soluble Salts and Geologic Age.—There is no consistent relationship between the amount or kind of water-soluble salts and the geologic age of the samples studied which cannot be ascribed to the mineralogic character of the samples.

HYDROGEN ION CONCENTRATION OF LEACHES.

The hydrogen ion concentration of the leaches from all samples listed in Table 1 was determined with an electric pH meter. The average pH of the limestone leaches was 7.9 with a range between 7.0 and 8.3. For dolomite leaches the average was 8.46 and the range 8.05 to 8.74. The data show that the leaches from the limestones were generally somewhat less basic than those from the dolomites, but some limestone and dolomite leaches were equally basic.

HYDROGEN SULFIDE IN LIMESTONES.

A few of the gray or dark gray limestones studied gave off a "fetid" or "oily" odor when they were crushed or broken. This phenomenon is relatively common to many Illinois gray or dark gray limestones that contain dark organic material, particularly those of Mississippian age, but it has not been observed in Illinois dolomites, most of which are light-colored. The fetid odor is also noticeable when limestone samples are treated with hydrochloric acid. Hydrogen sulfide was recognized as a component of the fetid odor. Because of its possible relation to the formation of water-soluble sulfates in limestones, a limited number of determinations were made of the amount of gas evolved when 1/2- to 1-inch pieces of the following samples were dissolved in hydrochloric acid.

Sample number	Weight percent H_2S
26. (Kinkaid limestone)	.002
25. (Glen Dean limestone)	.002
24. (Okaw limestone)	Trace
18. (Salem limestone)	.003
11. (Racine dolomite)	.000
(Ste. Genevieve oolite)	.012

The Ste. Genevieve oolite sample was almost black and was not tested for water-soluble salts. It was included because it gave a very strong fetid odor when broken. The Racine dolomite did not give off a fetid odor and was included for comparison.

Calcite which gives off the odor of hydrogen sulfide when broken has been called "fetid calcite" or "Stinkkalk," and the sulfide is said to be released from fluid inclusions.[9] Lucas [10] ascribes the odor of foul smelling limestones to "a water soluble ammoniacal salt of a volatile acid, containing phosphorous but no sulfur," probably trapped in the calcite crystals.

PHYSICAL OCCURRENCE OF WATER-SOLUBLE SALTS.

Evidence on the physical mode of occurrence of the water-soluble salts is partly inferred. The general conclusion is that much of the calcium and sulfate (excluding calcium dissolved from calcite and dolomite) probably occurs as

[9] Palache, Chas., et al., Dana's System of Mineralogy, 7th ed., Vol. II, p. 153, 1951.

[10] Lucas, Gabriel, Preliminary results of a study of the odorous products of foul-smelling limestones: Compt, rend., vol. 234, pp. 121–123, 1952. Quotation from Chem. Abs., vol. 46, No. 9, May 10, 1952, 3920.

intergranular solid calcium sulfate with magnesium sulfate possibly occurring in the same manner. However, the sodium, potassium, and chlorides, together with some calcium, magnesium, and sulfate, are probably present primarily in solution in intragranular fluid inclusions. The bases for these conclusions follow.

Thin Sections.—Microscopic examination, with up to 1,500 times magnification, of thin sections of 19 of the limestones and dolomites otherwise investigated revealed the presence of numerous inclusions (Fig. 1). They could also be seen in minute fragments of the rocks. The inclusions are transparent and contain no recognizable vacuoles; whether they were fluid or gaseous could not be determined by inspection. They are not solid, judging from the absence of specks or cleavage lines in them. No inclusions were observed whose walls were lined with crystals such as might result from the evaporation of a

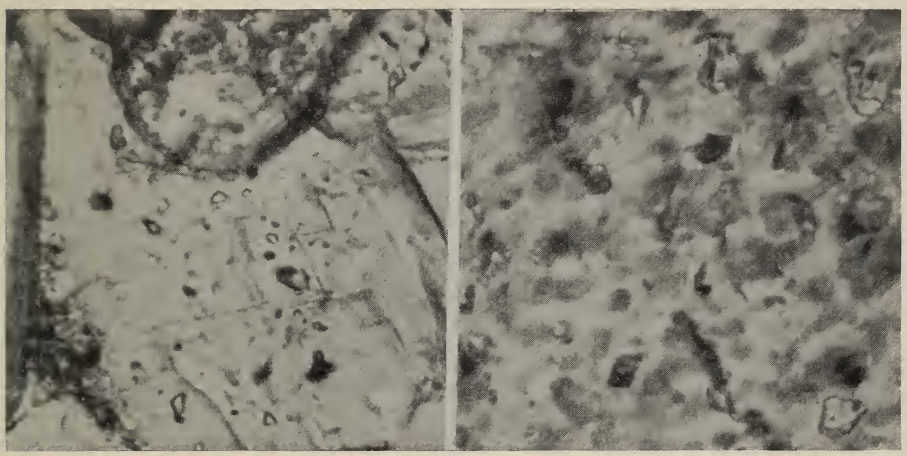

FIG. 1. Fluid inclusions in a thin section of Kimmswick limestone (left) and of Oneota dolomite (right). About 875 ×.

liquid. Data regarding the approximate size and abundance of the inclusions which could be identified with reasonable certainty are given in Table 6. It is to be noted that dolomites commonly contain a greater number of inclusions than limestones, but the inclusions are slightly smaller.

No crystals of gypsum, anhydrite, or halite, whose presence might possibly be expected from the soluble salt data, were noted in the thin sections. Because the thin sections were ground in water, such minerals might have dissolved in the process, but the sections had no holes showing the outlines of crystals of these minerals. Some sections were purposely left relatively thick in hope of protecting from solution any highly soluble minerals that might be present, but no such minerals were observed in the thick sections.

Decrepitation.—Differential thermal analysis apparatus was used in several unsuccessful attempts to determine whether a number of the samples gave

off water at temperatures above 110°. There were no significant anomalies, but a number of grains of some of the samples jumped out of the container block of the thermal analysis apparatus during the heating. As this phenomenon could have been caused by the explosion of water-filled inclusions, or possibly gas-filled inclusions, it was investigated further.

On a 5½-inch diameter round flat porcelain plate, concentric circles were drawn with radii of ½, 1, 1½, and 2 inches from the center. Four sectors, lying at 90 degrees to each other, were also drawn with a 1-inch chord on the rim of the plate. A small conical pile of limestone or dolomite grains was

TABLE 6.

ESTIMATE OF NUMBER AND SIZE OF INCLUSIONS TWO MICRONS OR MORE IN DIAMETER.

Sample	Number per 400 square microns	Common diameter —microns
27. Brereton limestone	2	2
26. Kinkaid limestone	3	2
24. Okaw limestone	4	3
23. Ste. Genevieve limestone, coarse grained	4	3
22. Ste. Genevieve limestone, fine grained	5	3
21. St. Louis limestone*		
18. Salem limestone	5	3
17. Burlington limestone, coarse grained	3	3
16. Burlington limestone, fine grained	6	3
15. Wapsipinicon limestone*		
13. Bailey limestone	1	2
11. Niagaran dolomite, medium grained	7	2
9. Niagaran dolomite, fine grained	7	2
8. Kimmswick limestone	6	2 and 4
6. Galena dolomite	5	3
4. McGregor dolomite	6	3
3. Shakopee dolomite	2	2
2. Oneota dolomite	7	2
1. Trempealeau dolomite	6	2
Avg. limestones	3.9	2.8
Avg. dolomites	5.7	2.3

* Inclusions present but too minute to measure or count.

formed in the center of the plate by filling and then gently lifting from the plate a small paper cylinder having a volume of .35 cc and holding .4 grams of 60 by 65 mesh limestone particles. The plate was then heated in an electric oven to 500° C in 45 minutes. After decrepitation the number of grains within two of the opposing sectors was tabulated according to whether they lay between the 1/2 and 1-inch circles, the 1-inch and 1 1/2-inch circles, etc. After heating, the central pile of particles showed small crater-like pits, in varying degrees, apparently caused by the sudden decrepitation of a grain or grains. The abundance of these pits and the amount of flattening of the pile were also noted.

To determine whether fluid inclusions could produce the decrepitation mentioned above, a sample of Iceland spar from a dike-like vein [11] at Taos, New Mexico, was separated by microscopic examination into chips containing no inclusions and those containing readily evident fluid-filled inclusions. Sixty by 65 mesh fractions were prepared from each and were heated on porcelain plates. The central pile of inclusion-free spar remained unchanged; a number of grains were scattered from the pile of spar that contained inclusions. A sample of fluorspar of similar sieve size prepared from crystals lining a cavity and known to contain fluid inclusions was heated and a scattering of grains likewise occurred.

Sixty by 65 mesh samples prepared from calcite crystals growing in open cavities and from multigranular travertine formed in an open cavity, both from Illinois limestone deposits, were also heated. Scattering of grains from the central piles occurred in both cases but was the more marked for the travertine (Table 7).

From the foregoing experiments it was concluded that fluid inclusions could cause limestone and dolomite grains to scatter by decrepitation. The fact that travertine and crystals from cavity linings decrepitate probably eliminates as a cause of decrepitation possible stresses set up in the limestones or dolomites during burial by other sediments. It is unlikely that the inclusions are gaseous because limestones and dolomites are formed in water and because the pressure increase set up by gaseous inclusions under the conditions of the decrepitation tests would be roughly only twice atmospheric pressure. This does not appear to be adequate to cause the observed decrepitation.

One further factor is involved in determining the significance of the decrepitation of the limestone and dolomite grains, namely the decrepitation of coarsely crystalline calcite, and presumably dolomite, resulting from their differential thermal expansion when heated. Frankel [12] experimented with crystalline calcite from a fissure vein and found that pieces of the calcite passing through a 3/8-inch screen did not decrepitate to "any marked degree" when heated to 400° C, but that larger pieces decrepitated "with violence." He ascribes decrepitation to the "great difference in thermal expansion along different directions in the crystal."

To what extent differential thermal expansion produced decrepitation of the limestone and dolomite grains of this study is uncertain but it is believed to be minor. As mentioned above, inclusion-free 60 by 65 mesh Iceland spar did not decrepitate, and Frankel's work suggests that decrepitation due to thermal expansion is primarily a phenomenon of coarse particles.

In further studies of limestones, samples were crushed and sieved to various particle sizes, and the sieve separates were heated to determine whether they would decrepitate and therefore might be judged to contain fluid inclusions. Results are given in Table 7 with the number of scattered grains calculated in "grains per square inch" for purposes of comparison. The 60 by 65 mesh

[11] Kelley, V. C., Iceland Spar in New Mexico: American Mineralogist, vol. 25, no. 3, p. 359, May 17, 1940.

[12] Frankel, J. J., The burning of coarsely crystalline calcite: Dept. of Mines, Union of S. Africa, Bull. 2, 1937, pp. 1–4.

TABLE 7.

DECREPITATION DATA.

Sample no.	Formation	Grain size	Sieve size of particles tested, mesh	Number of grains per sq. in.				Character of central pile after heating	Water soluble salts,* percent
				Distance from center of plate					
				½–1″	1–1½″	1½–2″	2–2¾″		
21	St. Louis limestone	Fine	60×65	255	64	39	24	Slightly flattened; a few pits	.020
27	Brereton limestone†	Fine	60×65	14	3	2	1	Not noticeably disturbed	.182
8	Kimmswick limestone	Coarse	60×65	890	280	135	33	Much flattened; pits numerous	.266
17	Burlington limestone	Coarse	60×65	675	260	165	72	Much flattened; pits numerous	.051
9	Racine dolomite	Fine	60×65	105	80	60	57	Slightly disturbed	.098
11	Racine dolomite	Medium	60×65	340	84	33	15	Slightly flattened; a few pits	.139
	Racine dolomite sand‡	Medium	60×65	Central pile completely scattered; much of sample on floor of oven					
2	Oneota dolomite	Medium	60×65	Central pile completely scattered; much of sample on floor of oven					.125
1	Trempealeau	Medium	60×65	215	72	21	8	Slightly flattened; a few pits	.059
	Travertine§	—	60×65	57	24	9	3	Very slightly flattened; a few pits	
	Calcite‖	—	60×65	36	8	3	2	Very slightly flattened; a few pits	
8	Kimmswick limestone	Coarse	100×150	425	100	33	17	Slightly flattened; pits moderately common	.266
2	Oneota dolomite	Medium	100×150	1,400	600	300	115	Flattened; numerous pits	.125
8	Kimmswick limestone	Coarse	270×325	No scattering					.266
2	Oneota dolomite	Medium	270×325	Very slight scattering					.125
8	Kimmswick limestone	Coarse	14×20	22	6	1	1	Flattened	.266
2	Oneota dolomite	Medium	14×20	Central pile largely scattered; much of sample on floor of oven					.125

* From column D, Table 2.
† Argillaceous.
‖ Large crystals from open cavity.
‡ From Spring Hill, Illinois.
§ Multi-crystalline; from open cavity.

particles of Oneota dolomite, sample 2, gave the maximum decrepitation of all samples on which leach data were determined; the central pile completely disappeared and the dolomite particles were scattered throughout the oven. No significant grain count could be made.

A 60 by 65 mesh fraction obtained by screening dolomite sand formed by natural disintegration of a high purity dolomite near Spring Hill, Illinois, into its component crystal particles was also tested to determine whether the agent causing decrepitation was inter- or intra-granular. It gave the greatest decrepitation of any of the samples, suggesting that an intra-granular agent was responsible.

The data in Table 7 regarding limestones, samples 21, 27, 8, and 17, suggest that coarsely crystalline limestones decrepitate more than finely crystalline rock, and that impure limestones probably decrepitate only slightly. The same relation between grain size and the decrepitation of dolomites seems to hold. No well demonstrated relationship is shown between the amount of soluble salts, as indicated by the totals of the chemical analyses of the leaches, and the degree of decrepitation.

Table 7 also gives data on the amount of decrepitation resulting when various-sized particles of Kimmswick limestone and Oneota dolomite were heated. The 14 by 20 mesh (1.68 by .833 mm) fraction and the 60 by 65 mesh (2.46 by 2.08 mm) fraction of the Oneota dolomite decrepitated to such an extent that the central pile was destroyed and the grains scattered about the oven. The 100 by 150 mesh (.147 by .104 mm) fraction scattered notably but remained largely on the porcelain plate. The 270 by 325 mesh (.053 by .044 mm) fraction scattered only slightly. The Kimmswick limestone tests showed the same general trend, with amount of decrepitation greatest in the 60 by 65 mesh fraction and no scattering of the 270 by 325 mesh grains.

The reasons for the foregoing are not fully understood. The fine grinding in preparing the 270 by 325 mesh fraction may have set up strains in the limestone and dolomite grains which allowed relatively easy escape of water vapor when the samples were heated. Or the small particles may have too little resistance to disruption to decrepitate violently. There appears to be an optimum relation between particle size and amount of grain scattering. This optimum is around 60 by 65 mesh for both the Kimmswick and Oneota samples.

Examination, after heating, of some of the samples disclosed that many of the particles displaced from the central pile were cracked, although still intact. Also numerous small cleavage blocks or flakes had been produced from the medium or coarsely crystalline samples. Many of these particles were badly cracked and some had small surficial pits which looked as though they had been formed by explosion of inclusions.

Some data on the temperatures at which maximum decrepitation occurred were obtained by periodic inspection of the samples during heating. A range of 325 and 425° C was indicated. These temperatures are considerably above the probable formation temperature of the limestones and dolomites from which the samples were prepared and the discrepancy suggests that the data are unreliable in this connection. A similar anomalous condition was found by

Peach for the decrepitation temperature of pegmatite calcite.[13] The sample of fluorspar mentioned above gave maximum decrepitation at about 325° C as against formation temperatures of 80 to 100° C which were determined by tests involving the temperatures of the disappearance of vacuoles.[14]

On the assumption that decrepitation is caused by fluid inclusions, the following experiment was carried out to determine the composition of the inclusions. A sample of Oneota dolomite was ground to 20 by 100 mesh and washed for 10 minutes with distilled water and then dried. It was then put through the decrepitation procedure and leached with distilled water for 10 minutes. The leach solids from this operation proved upon x-ray examination to be principally NaCl and $CaSO_4$ in about equal amounts. This suggests that both these salts came from inclusions.

A further experiment was made in an attempt to localize the sulfates. Seventy-five gram samples of 20 by 65, 65 by 150 and minus 150 mesh Oneota dolomite and of 20 by 65 and 65 by 150 mesh Kimmswick limestone were allowed to soak for 7 days in distilled water, which was changed daily. Two hundred cc of water were used on the seventh day, and 1,000 cc were used before that. The seventh-day waters were tested for sulfates with $BaCl_2$ and found to contain none. The samples were then dried and decrepitated. Thereafter they were again soaked in 200 cc of distilled water. This was then tested for sulfate, which was found in the water of all samples. The amount of sulfate in the leach water from the 20 by 65 mesh fractions of both the Oneota and Kimmswick was a little larger than the amount from the 65 by 150 mesh fractions, but the amount from the minus 150 mesh Oneota dolomite is estimated to have been roughly 5 times greater than that from the coarser fractions of the Oneota.

Several interpretations of the above data are possible, but if the seven-day washing of the samples removed all or most of the intergrain sulfate, as seems especially likely in the case of the minus 150 mesh powder, then it follows that the sulfate in the leaches after decrepitation was derived mainly from fluid inclusions which were disrupted during heating.

Fetid Limestone.—As mentioned above, the odor of fetid calcite has been ascribed to liquid inclusions containing hydrogen sulfide. The fetid odor of some of the limestones studied in this investigation therefore seems logically ascribable at least in part to the presence of fluid inclusions.

Efflorescence.—The presence in building stone of salts that will produce efflorescence may often be detected by immersing the lower part of a piece of the stone in distilled water, so that the water can work up through the specimen and evaporate at its upper surface where the efflorescence accumulates. This test was made on samples 5, 8, 15, 17, 18, 22, and 26. All these samples except sample 26 yielded some, though mostly very little, efflorescence. The character of the efflorescences as revealed by x-ray diffraction studies was as follows:

[13] Peach, P. A., Geothermometry of some pegmatite minerals of Iola, Ontario: Jour. Geol., vol. 59, no. 1, pp. 35–37, Jan. 1951.

[14] Grogan, R. M., and Shrode, R. S., Formation temperatures of southern Illinois fluorite as determined from fluid inclusions: Amer. Mineralogist, vol. 37, pp. 555–566, 1952.

Sample 5, Galena dolomite, calcium sulfate sub-hydrate,
Sample 8, Kimmswick limestone, gypsum,
Sample 15, Wapsipinicon limestone, calcite, dolomite and gypsum,
Sample 17, Burlington limestone, sodium chloride,
Sample 18, Salem limestone, calcium sulfate sub-hydrate,
Sample 22, Ste. Genevieve oolite, gypsum.

Some of the writers mentioned at the beginning of this paper found calcium and magnesium sulfates to be the principle components of the natural and experimental efflorescences of limestones; traces of chlorides were recorded in some.

The foregoing suggests that the sulfates in the samples studied were, in part at least, lodged along the water-permeable avenues of the stone (that is in pores or between crystals), and in dry specimens occur as solids. Conversely, as chloride was found in the efflorescence of only one sample, it seems probable that chlorides generally occur within the crystals where they are relatively inaccessible to the water.

Dolomite Sand.—The weathered surfaces of an exposure of very pure Racine formation reef-type dolomite in a quarry near Spring Hill, Illinois, are coated with 4 or 5 inches of loosely cemented, cream-colored dolomite sand weathered from the parent dolomite. A sample of the sand and a sample of the solid fresh parent dolomite were obtained. The sand sample, after thorough washing in distilled water to remove adhering substances, and the solid dolomite sample were leached by the procedure outlined above. The amounts of leach solids obtained from the samples were practically identical, suggesting that no great amount of water-soluble salts were held between the crystals of the solid dolomite and indicating that leach solids in the amount of 0.17 percent were derived largely or entirely from within the crystals of the dolomite sand.

X-ray data on the leach solids from the two samples were essentially the same. Only a small quantity of calcium sulfate was present. This is another line of evidence suggesting that the bulk of the water-soluble salts, excluding calcium sulfate, is contained within crystals.

ECONOMIC SIGNIFICANCE.

The presence, amount, and probable mode of occurrence of soluble salts in limestones and dolomites bear on a number of commercial uses. Though the weight percent of the water-soluble salts is small, the figures assume new meaning when converted to pounds per ton. Thus 0.2 percent would be equivalent to 4 pounds per ton or about 8 pounds per cubic yard. Obviously the salts will influence efflorescence and possibly the durability of building stone. Likewise they may well affect the hydrogen ion concentration of aqueous or other suspensions of limestone or dolomite powders, and may influence the character of mixtures such as putty. Some leach solids were observed to be sticky, especially in humid weather, presumably owing to the absorption of moisture. This characteristic may possibly tend to cause coating of the linings and balls of mills used to pulverize limestones or dolomites and might influence

the "flowability" of limestone and dolomite powders. As little as .10 percent of sodium chloride, and probably other chlorides, has been shown to modify the thermal decomposition characteristics of dolomites [15] and the salts thus may bear on the properties of these rocks during burning to lime. Lime burned with salt is said to slake better than that burned without salt.[16] The abundance and size of inclusions may likewise have an influence on the lime-making characteristics of limestone or dolomite and on the physical structure of burned lime. Water-soluble salts and the H_2S content of fetid limestones likewise merit consideration as possibly affecting the formation or localization of ore deposits.

Illinois Geological Survey,
Urbana, Ill.,
Dec. 22, 1952.

[15] Graf, Donald F., personal communication and Preliminary report on the variations in differential thermal curves of low-iron dolomite: American Mineralogist, vol. 37, nos. 1 and 2, pp. 1–27, Jan.-Feb. 1952.

[16] Ohno, Y., and Matsouka, Limestone, lime and slaked lime: II.: Jour. Ceram. Assn. Japan, vol. 59, no. 662, pp. 341–46, 1951. Cer. Abs., vol. 35, no. 1, p. 2, Jan. 1952.

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